Petrochemistry of Coal Ash Slags. 1. Formation of Melilite and a High Temperature Glass from a Calcium-Rich, Silica-Deficient Slag.

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The Grand Forks Energy Research Center (GFERC) of the Energy Research and Development Administration is conducting pilot plant studies of a fixed-bed slagging coal gasification process. The pilot plant was originally operated from 1958-1965 by the Bureau of Mines. The design and operation of the gasifier and the Bureau of Mines test results have been documented (1,2). Recent papers (3,4) have described the program objectives for the reactivated plant and have presented some preliminary results.

A schematic diagram of the gasifier is shown in Figure 1. Lignite or subbituminous coal is reacted with steam and oxygen at pressures to 27 atmospheres psig and at hearth zone temperatures exceeding 1650° C. A gas mixture is produced of which 90% is carbon monoxide and hydrogen at 2:1 ratio and the balance is composed of methane, carbon dioxide, and nitrogen. The hearth zone temperatures are maintained sufficiently high to cause melting of the ash. The molten slag drains into a water quench bath through a taphole in the hearth. Maintaining a steady flow of slag is crucial to the successful operation of the gasifier, since a build-up of slag on the hearth or a plug forming in the taphole will result in a premature shutdown of the test.

The petrochemistry of the slag is of considerable importance as a factor in hearth section design. Refractory selection will depend in part upon the chemical relationship between slag constituents and the refractories. If a phase transformation in the slag should produce a liquid having a composition well outside the design specifications, a rapid chemical degradation of the refractory structures could occur. The temperature dependence of slag viscosity is a function of slag composition. Since design of slag discharge orifices will be influenced in part by the expected viscosity range, viscosity changes caused by corresponding composition changes could alter slag flow characteristics.

Additional interest in slag petrochemistry arises from a similarity of slag compositions to naturally-occurring silicate melts. Thus the slagging operations in the gasifier can provide opportunities for studies of igneous rock petrology.

During operation, the slag is removed from the gasifier by periodically discharging the slag lock. The discharged slag is recovered as black, glassy granules (Fig. 2). In some tests the slag has been found to contain structures of

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unusual or atypical appearance. Samples of these are retained for detailed chemical and petrographic analysis. It is of particular concern to identify the phases formed, to determine or suggest the mechanism of the phase separation, and to predict the effect on such parameters as refractory attack, slag viscosity, and heat transfer.

The current series of tests in the GFERC gasifier uses lignite from the Indianhead mine of the North American Coal Company near Zap, North Dakota. Slag analyses are done using x-ray fluorescence. The analysis of the bulk slag varies slightly from run to run. Table 1 shows the slag analysis for a recent test and the range of observed values.

TABLE 1. Product Slag Analysis, Indianhead Lignite.

Oxides	Wt.,%	Range, %
SiO_2	39.5	31.1 - 39.7
Al_2O_3	13.6	11.8 - 13.6
Fe_2O_3	11.0	4.4 - 11.4
TiO_2	0.7	0.4 - 0.7
P_2O_5	0.3	0.3 - 0.6
CaO	17.9	17.9 - 33.7
MgO	5.3	5.3 - 7.4
Na_2O	6.6	0.1 - 10.5
K_2O	1.0	0.6 - 1.0
SO_3	4.1	1.9 - 4.1
TOTAL	100.0	

The composition is similar to that of a calcium-rich pyroxene.

Figure 3 shows a specimen of two-layered nodules recovered from the product slag of an early test (No. RA-4) in the current program. Table 2 shows the results of analysis of the inner and outer layers of the nodules, as well as the analysis of a bulk sample of the slag.

TABLE 2. Analyses of Regions of Indianhead Slag Nodules, Test RA-4

	Weight Percent		
	Inner Layer	Outer Layer	Bulk Sample
SiO_2	65.0	36.6	38.2
Al_2O_3	19.3	13.6	12.7
Fe_2O_3	5.8	13.0	8.0
TiO_2	0.9	0.7	0.6
P_2O_5	0.1	0.4	0.5
CaO	1.7	20.6	24.3
MgO	2.6	5.6	6.4
Na_2O	1.4	5.8	3.5
K_2O	2.9	0.8	0.9
SO_3	0.2	3.0	3.0
TOTAL	99.9	100.1	98.1

A thin section of one of these nodules is shown in Figure 4. Optical and x-ray diffraction study shows that the inner material is a vesicular glass with a small amount of disseminated quartz grains or fragments. The vesicles vary in size across the thin-sectioned chips, typically occurring in zones of smaller (0.01 mm) and larger (0.04 mm) approximate average diameter. In addition to the vesicles, numerous similar, spherical structures with pale tan color are present. These often contain or partly contain quartz grains. The outer layer of the nodules is very similar to the original slag.

Figure 5 shows a portion of a SiO_2-CaO-MgO ternary slice through the SiO_2-CaO-MgO-Al_2O_3 quarternary system, at 15 pct Al_2O_3. (Points are plotted on the basis of SiO_2 + CaO + MgO + Al_2O_3 = 100 pct). The composition of the inner layer lies in the cristobalite field, while both the outer layer and bulk slag compositions lie in the pyroxene field. The fact that crystallization of the inner layer was not more pronounced is very likely due to undercooling, since reported (5) slag discharge temperatures of 2300° F (1260° C) are less than 100° C above the fluid temperature of Indianhead slag.

The three-layered nodules were recovered from the slag in a more recent test (RA-7). The analysis of each layer is given in Table 3, along with an analysis of the bulk slag.

TABLE 3. Analyses of Regions of Indianhead Slag Nodules, Test RA-7

	Inner Layer	Middle Layer	Outer Layer	Bulk Sample
SiO_2	36.6	37.8	39.2	33.1
Al_2O_3	10.2	8.9	12.5	13.1
TiO_2	0.3	0.3	0.5	0.5
P_2O_5	0.5	0.5	0.5	0.6
CaO	40.5	38.7	31.1	22.6
MgO	7.9	9.5	6.8	5.4
Na_2O	0.3	0.5	1.2	6.1
K_2O	0.3	0.3	0.6	0.8
SO_3	3.1	2.5	1.4	2.4
Fe_2O_3	0.2	1.0	6.1	11.4
TOTAL	99.9	100.0	99.9	96.0

Thin section photographs of a three-layered nodule are shown in Figures 6 and 7. Optical and x-ray diffraction data show that the inner layers contain abundant melilite while the outer core is a glass. Melilite occurs as two types of clusters of radiating, zoned crystals. One type has zoning produced by dark, reddish cores, probably resulting from abundant iron-rich inclusions and exhibits a well developed dendritic intergrowth texture, probably from quenching. The second type of melilite has zoning shown by birefringence characteristics, probably from oscillatory or reverse chemical zoning and subhedral to euhedral crystal form.

In both cases these phase transformations can be related to temperature fluctuations in the gasifier hearth. Hearth zone temperatures are measured by a thermocouple mounted on the bottom of the hearth plate, and another in the gasifier wall approximately 5-1/2 feet above the hearth. Figures 8 and 9 show the two temperatures as a function of time for tests RA-4 and RA-7, as well as test RA-8, in which no slag phase separation was observed. Temperature data from RA-4 and RA-7 show sharp fluctuations, whereas the data from RA-8 show relatively stable temperatures.

The slag-refractory chemistry was found not to be significantly affected by either phase transformation described here. The slags have been characterized by calculating the base to acid ratio:

$$B/A = \frac{CaO + MgO + Na_2O + K_2O + Fe_2O_3}{SiO_2 + Al_2O_3 + TiO_2}$$

In the case of glass formation, the bulk slag has a basicity/acidity ratio of 0.84, while the liquid phase which would remain after formation of the glass nodules has a value of 0.90 (calculated from the analysis of the outer layer of the nodules). The corresponding values for the melilite formation are, respectively, 0.99 and 0.88. Neither situation represents a drastic change in slag basicity. Accelerated chemical degradation of hearth zone refractories is therefore an unlikely consequence of these phase transformations.

Changes in slag viscosity were estimated by calculating viscosities from a modified form of the Watt-Fereday equation (7),

$$\log \eta = 10^7 M/(T-150)^2 + C$$

where M and C are empirical constants which are functions of slag composition, the viscosity in poise, and the temperature in degrees Centigrade. Preliminary results from current GFERC research on adapting the Watt-Fereday equation to lignite slags were used to estimate order-of-magnitude viscosity changes. Viscosities were calculated from the bulk slag analysis and from the analysis of the outer layer of the nodules. Massive formation of melilite from Indianhead slag would leave a residual liquid having a calculated viscosity of 125 poise at 1350° C, while the calculated viscosity of the bulk slag is only 8 poise.

The change in slag viscosity will also affect hearth zone heat transfer relationships. For example, the calculation of the heat transfer coefficient between the slag and hearth plate is dependent upon the Grashof and Prandtl numbers for the flowing slag, both of which are functions of viscosity (8).

The results of this study show that the characteristics of the coal ash slag can be affected by temperature fluctuations in the gasifier hearth. Chemical, flow, and heat transfer behavior are all susceptible to change as a result.

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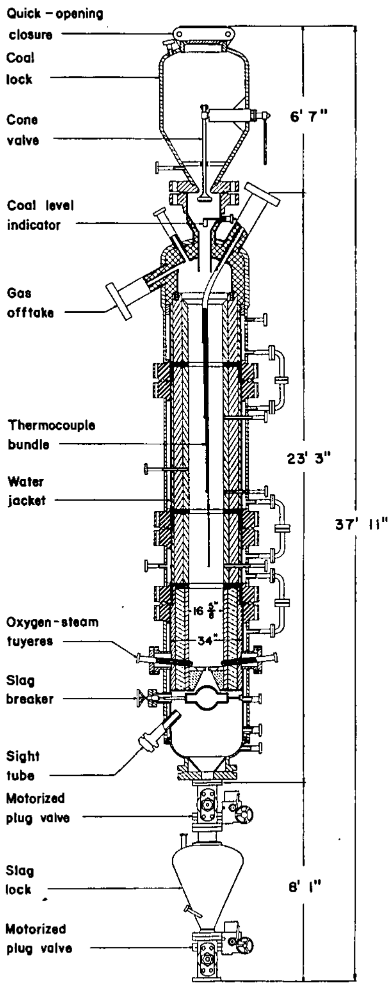

Figure 1. GFERC Gasifier

Figure 2. Typical Discharged Slag

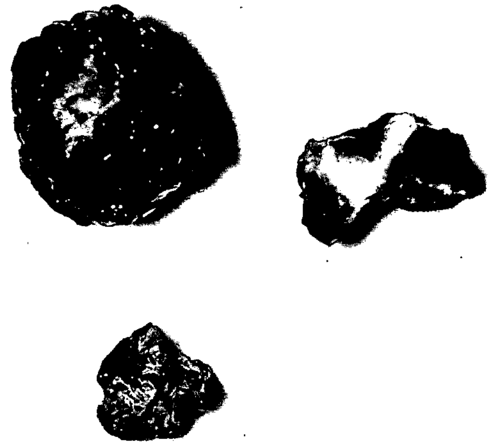

Figure 3. Two-layered Slag Nodules

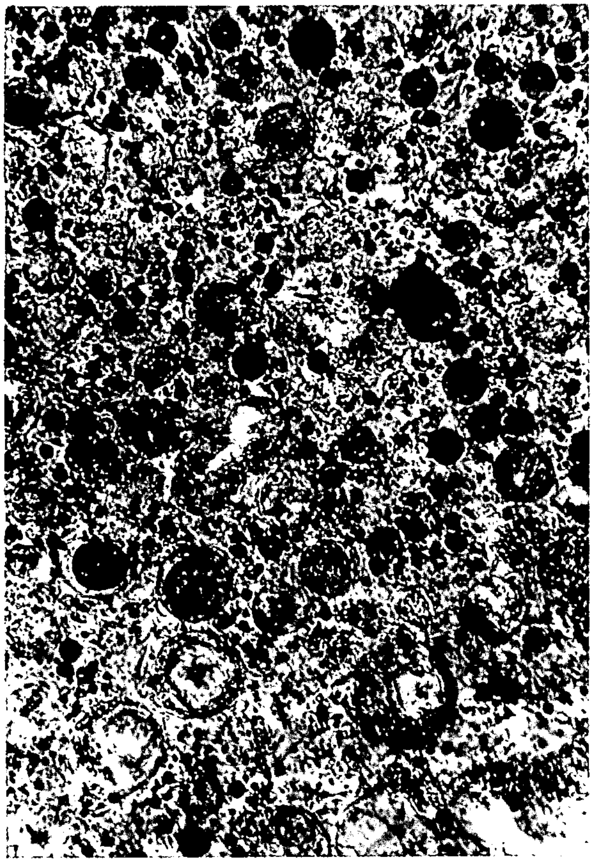

Figure 4. Thin section photograph of glassy part of two-layered nodule, showing two types of spherical structures. Photo taken using partly crossed polars; field of view, 0.7 mm.

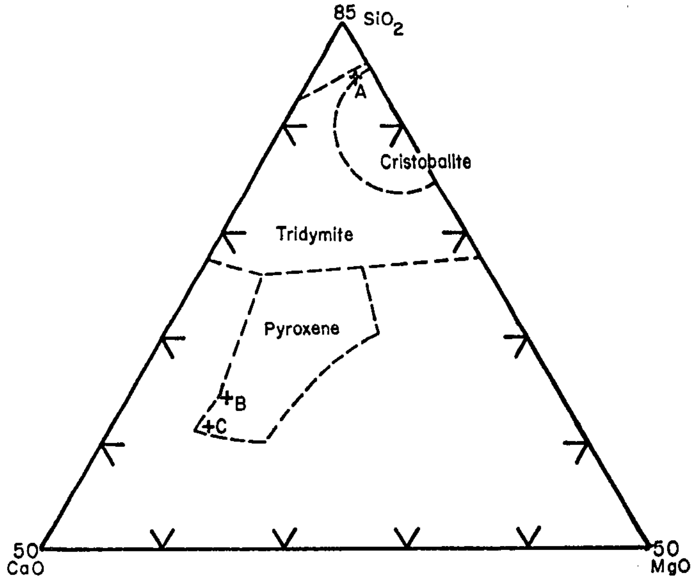

Figure 5. SiO_2-CaO-MgO Ternary at 15% Al_2O_3

A=Glass, B=Outer Layer of Nodule, C= Bulk Slag Composition

Figure 5. SiO_2-CaO-MgO Ternary slice of SiO_2-CaO-MgO-Al_2O_3 system. (15% Al_2O_5).

Figure 6. Melilite in three-layered nodules. Intergrowth of dendritic crystals with iron-rich cores. Photo taken in plane polarized light. Field of view, 3 mm.

Figure 7. Melilite in three-layered nodules. Crystal with chemical zoning shown by birefringence characteristics. Photo taken with crossed polars. Field of view, 1.2 mm.

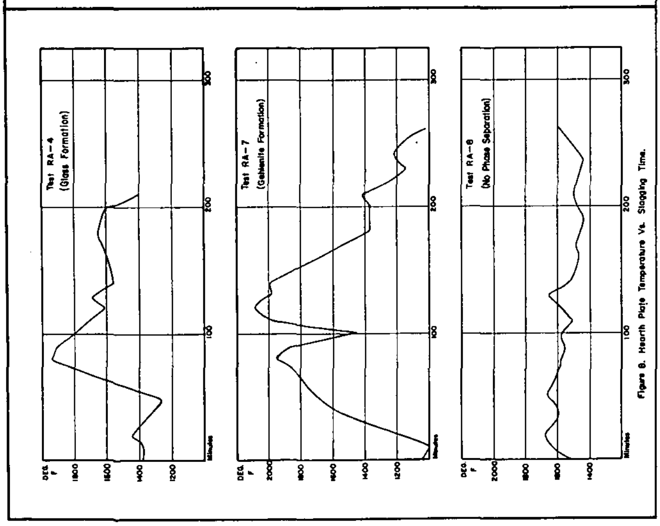

Figure 8. Hearth Plate Temperature Vs. Slagging Time.

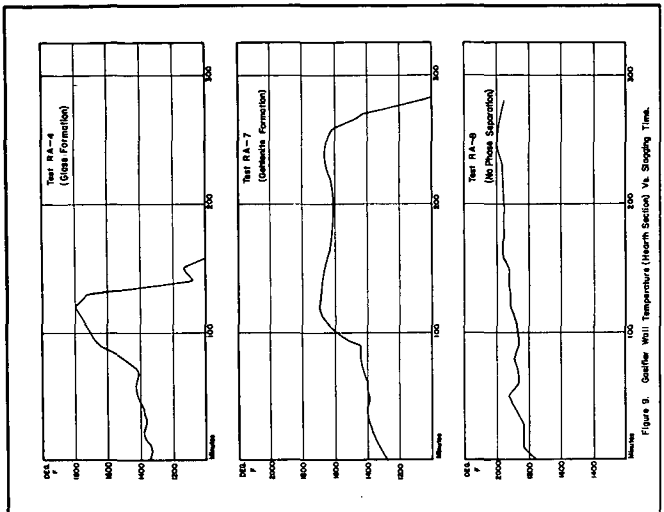

Figure 9. Gasifier Wall Temperature (Hearth Section) Vs. Slagging Time.